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FACILE SYNTHESES OF 2-ALKYL-2,3-DIHYDRO-2-METHYLBENZOFURAN DERIVATIVES

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Abstract: Various 2-alkyl-2,3-dihydro-2-methylbenzofurans **4** can be easily synthesized from 2-aryloxypropionic acid ethyl esters 1 by 3 steps in good yields.

2,3-Dihydrobenzofurans have been known as important intermediates in natural products[1] and pesticides chemistry.[2] Lots of studies were reported on the syntheses of 2,3-dihydrobenzofuran derivatives,[3] however, there were few reports on the syntheses of 2-alkyl-2,3-dihydro-2-methylbenzofurans except 2,3-dihydro-2,2-dimethylbenzofurans. 2,2-Dialkyl-2,3-dihydrobenzofurans could be directly prepared from phenols and 2,2-disubstituted aldehydes in the presence of strong acid with heating,[4] or from 2-hydroxybenzyl alcohol derivatives in the presence of an acid ion-exchange resin and molecular sieves.[5] Both of the reactions include the same intermediates, 2-hydroxybenzyl alcohol derivatives which should have dialkylmethyl group on benzylic carbon in order to form a

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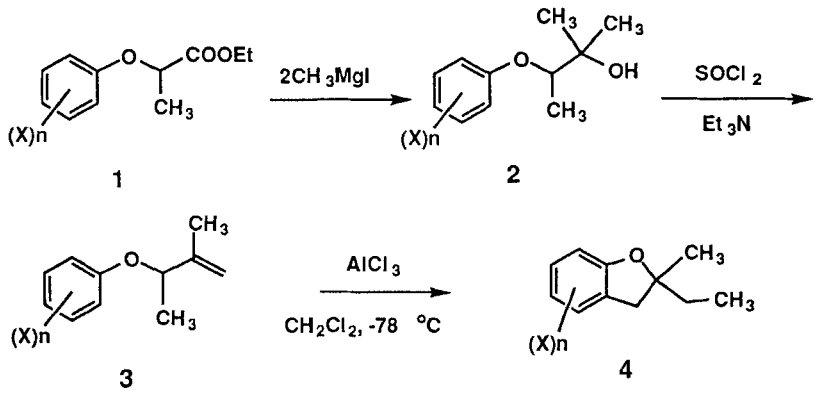
stable *tertiary* carbocation, and the yields of the benzofurans were not satisfactory. 2,3-Dihydro-2-ethyl-2-methylbenzofuran was obtained as a minor product from the reaction of 2-(β,γ-dimethylallyl)phenol with dichlorobis-(benzonitrile)-palladium (II).[6] 2-(2-Hydroxy-2-methylpropoxy)phenol which was prepared from catechol and 1-chloro-2-methyl-2-propanol could be cyclized to 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran by heating in the presence of a strong acid.[7]

In the previous paper,[8] we have described the facile procedures of the synthesis of 2,3-dihydro-2,2-dimethylbenzofurans from aryl methallyl ether involving aluminium chloride under very mild conditions. In continuation of this study, we herein wish to report a general method of preparing 2-alkyl-2,3-dihydro-2-methylbenzofurans. Initially, the one step cyclization reaction of *tertiary* alcohol **2** to benzofuran **4** catalyzed by a protonic acid such as sulfuric acid, polyphosphoric acid, or *p*-toluenesulfonic acid in toluene with heating were attempted, however, the precedent starting phenol was isolated as a major. Also Lewis acids such as $AlCl_3$, BF_3Et_2O and polymeric resin, Amberist-15 were examined as catalysts but we failed to isolate the benzofurans **4**. Eventually, we could develop a new procedure for preparing 2-alkyl-2,3-dihydro-2-methyl-benzofurans as followings.



Scheme 1

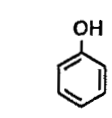
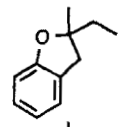
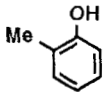
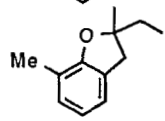
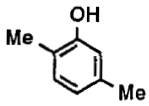
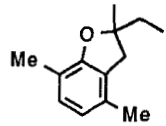
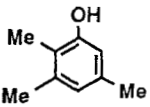
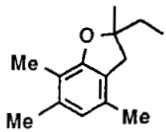
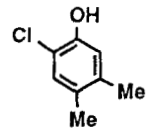
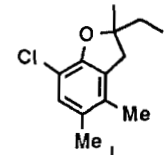
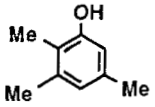
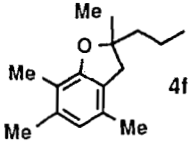
2-Aryloxypropionic acid ethyl esters **1**, which were prepared from the reaction of substituted phenols and ethyl 2-bromopropionate, were reacted with 2 equiv of methyl magnesium iodide to afford *tertiary* alchohols **2** as shown in Scheme 1. The *tertiary* alcohols **2** were easily dehydrated by the treatment of an equiv of thionyl chloride and 3 equiv of triethylamine to afford substituted allyl aryl ethers **3** in good yields. The substituted allyl aryl ethers **3** were converted to the 2,3-dihydro-2-ethyl-2-methylbenzofurans **4** by a tandem Claisen rearrangement-cyclization with aluminium chloride as catalyst in good yields. The compounds 1, **2**, **3**, and 4 were easily isolated by distillation under high vacuum. The representative results are shown in Table 1.

For dehydration of **2**, we have examined various acid halides with bases such as thionyl chloride, methanesulfonyl chloride, or *p*-toluenesulfonyl chloride with triethylamine or pyridine as a base, and the use of thionyl chloride with 3 equiv of triethylamine gave the best results. Interestingly, the dehydration of **2** afforded **3** having *exo* double bond predominantly without any detection of *endo* double bonded compound in the ^{1}H nmr spectrum. The structures of the final products, 2,3-dihydro-2-ethyl-2-methylbenzofurans **4** were easily identified by the C-2 ethyl group and C-3 protons which showed two doublets with large coupling constants (15-16 Hz) in the ^{1}H nmr spectra. In case of Entry 6 in Table 1, 2,3,5-trimethylphenol was reacted with ethyl 2-bromobutyrate instead of ethyl 2-bromopropionate to afford ethyl 2-(2,3,5-trimethylphenyl)oxybutyrate **1f**. By the analogous procedure, 2-methyl-2-propylbenzofuran derivative **4f** was obtained from **1f** in good yield. By the judgement of these results, our procedures are thought to be the most useful methods for the syntheses of various 2-alkyl-2,3-dihydro-2-methylbenzofurans.

EXPERIMENTAL

Materials and Instrument. All the starting materials and reagents were purchased from Aldrich and used without further purification. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer. ^{1}H *nmr spectra were*

Table 1. Synthesis of 2,3-Dihydro-2-Ethyl-2-Methylbenzofurans **4** from Substituted- Phenols.

Entry	Starting Material	Final Product (**4**)	Yield (%) [a]			
			1	**2**	**3**	**4**
1		 **4a**	81	94	71	63
2		 **4b**	83	97	69	64
3		 **4c**	80	92	67	68
4		 **4d**	88	87	72	81
5		 **4e**	89	93	75	82
6		 **4f**	79[b]	87	74	66

a. Isolated by distillation under high vacuum.

b. 2,3,5-Trimethylphenol was reacted with ethyl 2-bromobutyrate instead of ethyl 2-bromopropionate to afford **1f**, and the same procedures were applied for the syntheses of **2f**, **3f**, and **4f**.

obtained with a Varian GEMINI-200 using $CDCl_3$ as a solvent. All chemical shifts are reported in ppm downfield from internal tetramethylsilane and coupling constants (J) are given in Hz. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 mass spectrometer. High resolution mass spectra (HR/MS) were obtained on a Jeol JMX-DX-303 mass spectrophotometer. Chromatographic separations were carried out on a silica gel column (Merck silica gel 60).

General Procedure of the preparation of Ethyl 2-aryloxypropionate (1)

A mixture of substituted phenol (0.5 M), ethyl 2-bromopropionate (108.6 g, 0.6 M), and potassium carbonate (69.0 g, 0.5 M) in acetone-DMF solvent (acetone: 200ml, DMF: 40ml) was heated under reflux in the presence of cataytic amount of potassium iodide (1 g) until the phenol disappeared. The reaction mixture was poured into cold water (300 ml) and the organic layer was extracted with ethyl ether (300 ml). The organic layer was washed with 10 % NaOH solution, water, and brine. The ethreal layer was dried over anhydrous magnesium sulfate and concentrated to afford crude ethyl 2-aryloxypropionate 1 as a pale yellow oil. The oil was further purified by vacuum distillation to afford a colorless oil.

Ethyl 2-phenoxypropionate (1a)

Colorless oil (81 %). bp: 64 °C/0.4 torr; ^{1}H nmr ($CDCl_3$) δ 1.24 (t, J=7.0 Hz, 3H), 1.61 (d, J=6.8 Hz, 3H), 4.21 (q, J=7.0 Hz, 2H), 4.74 (q, J=6.8 Hz, 1H), 6.85-7.00 (m, 3H), 7.23-7.31 (m, 2H); MS (70 eV) m/z (rel. intensity) 195 (M^++1, 5.8), 194 (M^+, 27), 121 (100), 77 (29).

Ethyl 2-(2-methylphenyl)oxypropionate (1b)

Colorless oil (83 %). bp: 92 °C/0.3 torr; ^{1}H nmr ($CDCl_3$) δ 1.22 (t, J=7.0 Hz, 3H), 1.61 (d, J=6.6 Hz, 3H), 2.27 (s, 3H), 4.18 (q, J=7.0 Hz, 2H), 4.71 (q, J=6.6 Hz, 1H), 6.65-6.89 (m, 2H), 7.01-7.14 (m, 2H); IR (cm^{-1}) 2954, 1744, 1722, 1596, 1482, 1438, 1226, 1180, 1121, 1042, 745; MS (70 eV) m/z (rel. intensity) 209 (M^++1, 41), 208 (M^+, 100), 135 (100), 108 (25), 107 (38).

Ethyl 2-(2,5-dimethylphenyl)oxypropionate (1c)

Colorless oil (80 %). bp: 95-96 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 1.24 (t, J=6.8 Hz, 3H), 1.60 (d, J=6.8 Hz, 3H), 2.22 (s, 3H), 2.26 (s, 3H), 4.20 (q, J=6.8 Hz, 2H), 4.71 (q, J=6.8 Hz, 1H), 6.50 (s, 1H), 6.68 (d, 2H); IR (cm^{-1}) 3411, 2952, 1732, 1607, 1576, 1495, 1435, 1405, 1244, 1181, 1115, 1042, 847, 799; MS (70 eV) m/z (rel. intensity) 222 (M^+, 78), 149 (100), 122 (32), 121 (43), 105 (22).

Ethyl 2-(2,3,5-trimethylphenyl)oxypropionate (1d)

Colorless oil (89 %). bp: 108-110 °C/0.25 torr; ^{1}H nmr ($CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H), 1.60 (d, J=6.8 Hz, 3H), 2.15 (s, 3H), 2.21 (s, 3H), 2.23 (s, 3H), 4.21 (q, J=6.2 Hz, 2H), 4.69 (q, J=6.8 Hz, 1H), 6.40 (s, 1H), 6.62 (s, 1H); IR (cm^{-1}) 2891, 1747, 1721, 1607, 1573, 1454, 1434, 1255, 1181, 1130, 1091, 822, 629; MS (70 eV) m/z (rel. intensity) 237 (M^++1, 23), 236 (M^+, 100), 163 (100), 136 (85), 135 (100), 119 (75).

Ethyl 2-(2-chloro-4,5-dimethylphenyl)oxypropionate (1e)

Colorless oil (89 %). bp: 108-110 °C/0.25 torr; ^{1}H nmr ($CDCl_3$) δ 1.24 (t, J=7.0 Hz, 3H), 1.63 (d, J=7.0 Hz, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 4.20 (q, J=7.0 Hz, 2H), 4.68 (q, J=7.0 Hz, 1H), 6.67 (s, 1H), 7.08 (s, 1H); MS (70 eV) m/z (rel. intensity) 258 (M^++2, 38), 256 (M^+, 100), 183 (20).

Ethyl 2-(2,3,5-trimethylphenyl)oxybutyrate (1f)

A mixture of 2,3,5-trimethylphenol (68.1 g, 0.5 M), ethyl 2-bromobutyrate (117.0 g, 0.6 M), and potassium carbonate (69.0 g, 0.5 M) in acetone-DMF solvent (acetone: 200ml, DMF: 40ml) was heated under reflux in the presence of cataytic amount of potassium iodide (1 g) until the phenol disappeared. The reaction mixture was poured into cold water (300 ml) and the organic layer was extracted with ethyl ether (300 ml). The organic layer was washed with 10 % NaOH solution, water, and brine. The ethreal layer was dried over anhydrous magnesium sulfate and concentrated to afford crude ethyl 2-(2,3,5-trimethylphenyl)oxybutyrate **1f** as a pale yellow oil. The oil was further purified by vacuum distillation (118 °C/0.025 torr) to afford a colorless oil (93.3 g, 79%).

^{1}H nmr ($CDCl_3$) δ 1.07 (t, J=7.6 Hz, 3H), 1.22 (t, J=7.2 Hz, 3H), 1.88-1.98 (m, 2H), 2.16 (s, 3H), 2.20 (s, 3H), 2.21 (s, 3H), 4.21 (q, J=6.0 Hz, 2H), 4.48-4.69 (m, 1H), 6.36 (s, 1H), 6.59 (s, 1H); IR (cm^{-1}) 2945, 1748, 1726, 1575, 1438, 1290, 1262, 1184, 1141, 1107, 1018; MS (70 eV) m/z (rel. intensity) 251 (M^++1, 50), 250 (M^+, 100), 236 (26), 177 (61), 163 (29), 135 (24).

General Procedure of the preparation of 2-Aryloxy-1,1-dimethylpropanol (2)

To a suspension of magnesium turning (14.6 g, 0.6 M) in 200 ml of ether was added dropwise iodomethane (71.0 g, 0.5 M) in ether (100 ml) with occasional cooling. To the resulting methyl magnesium iodide solution was added dropwise ethyl 2-aryloxypropionate 1 (0.2 M) diluted with ether (50 ml) at room temperature. After the reaction completed, the reaction mixture was poured into ice-cold 2 N HCl solution (300 ml) with shaking. The organic layer was separated, washed with brine, dried over anhydrous magnesium sulfate, and concentrated to give pale yellow oil. The oil was distilled under vacuum to afford pure 2-aryloxy-1,1-dimethylpropanol **2** as a colorless oil.

1,1-Dimethyl-2-phenoxypropanol (2a)

Colorless oil (94 %). bp: 66 °C/0.025 torr; ^{1}H nmr ($CDCl_3$) δ 1.24 (d, J=6.4 Hz, 3H), 1.28 (s, 6H), 2.36 (s, 1H, -OH), 4.19 (q, J=6.4 Hz, 1H), 6.90-6.98 (m, 3H), 7.24-7.32 (m, 2H); MS (70 eV) m/z (rel. intensity) 180 (M^+, 23), 163 (30), 122 (71), 121 (29), 94 (100), 77 (29).

1,1-Dimethyl-2-(2-methylphenyl)oxypropanol (2b)

Colorless oil (97 %). bp: 82 °C/0.05 torr; ^{1}H nmr ($CDCl_3$) δ 1.19-1.29 (m, 9H), 2.21 (s, 3H), 2.40 (s, 1H, -OH), 4.20 (q, J=6.4 Hz, 1H), 6.78-6.87 (m, 2H), 7.02-7.19 (m, 2H); IR (cm^{-1}) 3397, 2949, 1596, 1485, 1365, 1234, 1114, 1062, 745; MS (70 eV) m/z (rel. intensity) 194 (M^+, 100), 177 (14), 136 (24), 108 (48).

1,1-Dimethyl-2-(2,5-dimethylphenyl)oxypropanol (2c)

Colorless oil (92 %). bp: 74 °C/0.005 torr; ^{1}H nmr ($CDCl_3$) δ 1.22 (d, J=6.2 Hz,

3H), 1.28 (s, 3H), 1.30 (s, 3H), 2.17 (s, 3H), 2.30 (s, 3H), 2.42 (s, 1H, -OH), 4.21 (q, J=6.4 Hz, 1H), 6.69-7.19 (m, 3H); IR (cm^{-1}) 3394, 2947, 1605, 1576, 1496, 1439, 1403, 1365, 1252, 1150, 1121, 1063; MS (70 eV) m/z (rel. intensity) 208 (M^+, 100), 191 (83), 122 (79).

1,1-Dimethyl-2-(2,3,5-trimethylphenyl)oxypropanol (2d)

Colorless oil (87 %). bp: 95-96 °C/0.025 torr; ^1H nmr ($CDCl_3$) δ 1.20 (d, J=7.5 Hz, 3H), 1.29 (s, 3H), 1.30 (s, 3H), 2.10 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 2.45 (s, 1H, -OH), 4.20 (q, J=7.5 Hz, 1H), 6.58 (s, 1H), 6.60 (s, 1H); IR (cm^{-1}) 3404, 2946, 1606, 1573, 1477, 1436, 1364, 1295, 1274, 1166, 1136, 1090, 943, 827; MS (70 eV) m/z (rel. intensity) 223 (M^++1, 12), 222 (M^+, 78), 164 (56), 163 (31), 136 (100), 121 (100), 105 (38).

2-(2-Chloro-4,5-dimethylphenyl)oxy-1,1-dimethylpropanol (2e)

Colorless oil (93 %). bp: 126-127 °C/0.05 torr; ^1H nmr ($CDCl_3$) δ 1.28 (d, J=6.8 Hz, 3H), 1.29 (s, 6H), 2.16 (s, 3H), 2.21 (s, 3H), 2.65 (s, 1H, -OH), 4.18 (q, J=6.4 Hz, 1H), 6.77 (s, 1H), 7.11 (s, 1H); IR (cm^{-1}) 3383, 2947, 1598, 1486, 1459, 1364, 1262, 1191, 1147, 1062, 687; MS (70 eV) m/z (rel. intensity) 244 (M^++2, 11.8), 242 (M^+, 5.7), 184 (9), 158 (33), 156 (100), 121 (24).

1,1-Dimethyl-2-(2,3,5-trimethylphenyl)oxybutanol (2f)

Colorless oil (87 %). bp: 122 °C/0.1 torr; ^1H nmr ($CDCl_3$) δ 0.94 (t, J=7.6 Hz, 3H), 1.25 (s, 6H), 1.62-1.78 (m, 2H), 2.12 (s, 3H), 2.21 (s, 3H), 2.26 (s, 3H), 2.60 (s, 1H, -OH), 4.05-4.12 (m, 1H), 6.55 (s, 1H), 6.64 (s, 1H); IR (cm^{-1}) 3354, 2943, 1575, 1454, 1370, 1302, 1137, 1097, 974, 826; MS (70 eV) m/z (rel. intensity) 236 (M^+, 94), 222 (24), 136 (100), 121 (30).

General Procedure of the preparation of 3-Aryloxy-2-methyl-1-butene (3)

To a cooled solution of 2-aryloxy-1,1-dimethylpropanol 2 (0.2 M) triethylamine (60.7 g, 0.6 M) in methylene chloride (50 ml) was added thionyl chloride (30.6 g, 0.22 M) very slowly at 0 °C. The reaction mixture was warmed to room temperature and stirred for 0.5 h at that temperature. The reaction mixture was

poured into cold water (100 ml) and extracted with ether (200 ml). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated to give pale yellow oil. The oil was distilled under vacuum to afford pure 3-aryloxy-2-methyl-1-butene **3** as a colorless oil.

2-Methyl-3-phenoxy-1-butene (3a)

Colorless oil (71 %). bp: 43 °C/0.025 torr; ^{1}H nmr ($CDCl_3$) δ 1.43 (d, J=6.4 Hz, 3H), 1.72 (s, 3H), 4.70 (q, J=6.6 Hz, 1H), 4.98 (m, 1H), 5.00 (m, 1H), 6.83-6.89 (m, 3H), 6.92-6.97 (m, 2H); IR (cm^{-1}) 3043, 2893, 1685, 1642, 1582, 1475, 1444, 1214, 1143, 1074, 992, 945, 900, 800, 748, 686; MS (70 eV) m/z (rel. intensity) 163 (M^++1, 27), 162 (M^+, 100), 94 (100), 69 (55).

2-Methyl-3-(2-methylphenyl)oxy-1-butene (3b)

Colorless oil (69 %). bp: 58 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 1.45 (d, J=6.6 Hz, 3H), 1.74 (s, 3H), 2.24 (s, 3H), 4.70 (q, J=6.6 Hz, 1H), 4.88 (m, 1H), 5.00 (m, 1H), 6.67-6.89 (m, 2H), 7.00-7.20 (m, 2H); IR (cm^{-1}) 2951, 1598, 1483, 1233, 1145, 1112, 745; MS (70 eV) m/z (rel. intensity) 176 (M^+, 85), 108 (100), 91 (31), 79 (29).

3-(2,5-Dimethylphenyl)oxy-2-methyl-1-butene (3c)

Colorless oil (67 %). bp: 70 °C/0.2 torr; ^{1}H nmr ($CDCl_3$) δ 1.42 (d, J=6.4 Hz, 3H), 1.74 (s, 3H), 2.19 (s, 3H), 2.26 (s, 3H), 4.71 (q, J=6.4 Hz, 1H), 4.85 (m, 1H), 5.00 (m, 1H), 6.60 (s, 1H), 6.61 (d, J=6.4 Hz, 1H), 6.98 (d, J=6.4 Hz, 1H); IR (cm^{-1}) 2948, 1642, 1607, 1576, 1495, 1248, 1151, 1120, 996, 895, 797; MS (70 eV) m/z (rel. intensity) 190 (M^+, 7), 122 (100), 107 (37), 91 (16).

2-Methyl-3-(2,3,5-trimethylphenyl)oxy-1-butene (3d)

Colorless oil (83 %). bp: 79-80 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 1.40 (d, J=6.4 Hz, 3H), 1.74 (d, J=1.0 Hz, 3H), 2.21 (s, 3H), 2.23 (s, 6H), 4.69 (q, J=6.4 Hz, 1H), 4.87 (m, 1H), 4.98 (m, 1H), 6.50 (s, 1H), 6.57 (s, 1H); IR (cm^{-1}) 2940, 1606, 1572, 1477, 1430, 1363, 1290, 1150, 1080, 967, 895, 826; MS (70 eV) m/z (rel. intensity) 205 (M^++1, 10), 204 (M^+, 65), 161 (36), 136 (100), 121 (78), 91 (32).

3-(2-Chloro-4,5-dimethylphenyl)oxy-2-methyl-1-butene (3e)

Colorless oil (85 %). bp: 74 °C/0.025 torr; ^{1}H nmr ($CDCl_3$) δ 1.47 (d, J=6.4 Hz,

3H), 1.76 (s, 3H), 2.13 (s, 3H), 2.17 (s, 3H), 4.71 (q, J=6.2 Hz, 1H), 4.88-4.99 (m, 2H), 6.69 (s, 1H), 7.08 (s, 1H); IR (cm^{-1}) 3047, 2896, 1597, 1487, 1439, 1380, 1260, 1193, 1149, 1073, 1042, 896; MS (70 eV) m/z (rel. intensity) 226 (M^++2, 7.3), 224 (M^+, 20.3), 158 (35), 156 (100), 121 (8).

2-Methyl-3-(2,3,5-trimethylphenyl)oxy-1-pentene (3f)

Colorless oil (74 %). bp: 67 °C/0.01 torr; ^1H nmr ($CDCl_3$) δ 0.97 (t, J=7.4 Hz, 3H), 1.73-1.78 (m, 2H), 1.71 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 4.39-4.46 (m, 1H), 4.87-5.00 (m, 1H), 4.98 (m, 2H), 6.48 (s, 1H), 6.56 (s, 1H); IR (cm^{-1}) 2938, 1574, 1479, 1440, 1302, 1275, 1150, 1098, 894, 825; MS (70 eV) m/z (rel. intensity) 218 (M^+, 40), 204 (22), 136 (100), 122 (32), 121 (34), 86 (50).

General Procedure of the preparation of 2,3-Dihydro-2-ethyl-2-methyl-benzofurans (4)

3-aryloxy-2-methyl-1-butene **3** (0.2 M) in anhydrous dichloromethane (150 ml) was cooled at -70 °C under nitrogen atmosphere. To this mixture was added slowly aluminium chloride (2.67 g, 0.02 M) over 15 min and the mixture was stirred at that temperature for 30 min. The reaction mixture was then slowly warmed up to room temperature. The brown reaction mixture was poured in several portions into an ice-cold water with stirring. The organic layer was separated, washed with brine twice, dried over magnesium sulfate, and concentrated to give a brown oil. The oil was distilled under vacuum to afford pure 2,3-dihydro-2-ethyl-2-methylbenzofurans **4** as a colorless oil.

2,3-Dihydro-2-ethyl-2-methylbenzofuran (4a)

Colorless oil (63 %). bp: °C/ torr; ^1H nmr ($CDCl_3$) δ 0.94 (t, J=7.4 Hz, 3H), 1.38 (s, 3H), 1.73 (q, J=7.4 Hz, 2H), 2.84 (d, J=15.6 Hz, 1H), 3.02 (d, J=15.6 Hz, 1H), 6.69-6.81 (m, 2H), 7.02-7.12 (m, 2H); IR (cm^{-1}) 2903, 1630, 1473, 1241, 880, 744; MS (70 eV) m/z (rel. intensity) 162 (M^+, 100), 147 (36), 133 (95), 107 (21), 105 (23).

2,3-Dihydro-2,7-dimethyl-2-ethylbenzofuran (4b)

Colorless oil (64 %). bp: °C/ torr; ^{1}H nmr ($CDCl_3$) δ 0.94 (t, J=7.6 Hz, 3H), 1.39 (s, 3H), 1.70 (q, J=7.4 Hz, 2H), 2.18 (s, 3H), 2.86 (d, J=15.6 Hz, 1H), 3.03 (d, J=15.6 Hz, 1H), 6.65-6.72 (m, 1H), 6.86-6.94 (m, 2H); IR (cm^{-1}) 2930, 1592, 1455, 1369, 1254, 1219, 1125, 824, 753; MS (70 eV) m/z (rel. intensity) 176 (M^+, 49), 161 (22), 147 (100), 121 (21), 119 (35).

2,3-Dihydro-2-ethyl-2,4,7-trimethylbenzofuran (4c)

Colorless oil (68 %). bp: 48 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H), 1.45 (s, 3H), 1.77 (q, J=7.4 Hz, 2H), 2.20 (s, 6H), 2.85 (d, J=15.4 Hz, 1H), 3.01 (d, J=15.4 Hz, 1H), 6.60 (d, J=7.4 Hz, 1H), 6.85 (d, J=7.4 Hz, 1H); IR (cm^{-1}) 2896, 1587, 1444, 1409, 1369, 1255, 1211, 1135, 1067, 950, 787; MS (70 eV) m/z (rel. intensity) 190 (M^+, 39), 162 (94), 161 (100), 134 (36), 133 (40), 91 (25).

2,3-Dihydro-2-ethyl-2,4,6,7-tetramethylbenzofuran (4d)

Colorless oil (81 %). bp: 68 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 0.96 (t, J=7.4 Hz, 3H), 1.40 (s, 3H), 1.73 (q, J=7.4 Hz, 2H), 2.08 (s, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 2.96 (d, J=15.4 Hz, 1H), 3.13 (d, J=15.4 Hz, 1H), 6.72 (s, 1H); IR (cm^{-1}) 2939, 1505, 1449, 1401, 1082, 911, 835; MS (70 eV) m/z (rel. intensity) 205 (M^++1, 15), 204 (M^+, 100), 175 (90), 136 (22).

7-Chloro-2,3-dihydro-2-ethyl-2,4,5-trimethylbenzofuran (4e)

Colorless oil (80 %). bp: 86 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.43 (s, 3H), 1.76 (q, J=7.4 Hz, 2H), 2.06 (s, 3H), 2.13 (s, 3H), 2.85 (d, J= 15.6 Hz, 1H), 3.03 (d, J=15.6 Hz, 1H), 6.86 (s, 1H); IR (cm^{-1}) 2939, 1594, 1440, 1369, 1270, 1229, 1037, 926, 856, 826; MS (70 eV) m/z (rel. intensity) 226 (M^++ 2, 34), 224 (M^+, 100), 195 (72).

2,3-Dihydro-2-propyl-2,4,6,7-tetramethylbenzofuran (4f)

Colorless oil (66 %). bp: 88 °C/0.1 torr; ^{1}H nmr ($CDCl_3$) δ 0.97 (t, J=7.4 Hz, 3H), 1.41 (s, 3H), 1.40-1.48 (m, 2H), 1.63-1.73 (m, 2H), 2.05 (s, 3H), 2.13 (s, 3H), 2.20 (s, 3H), 2.82 (d, J=15.6 Hz, 1H), 2.95 (d, J=15.6 Hz, 1H), 6.48 (s, 1H); IR (cm^{-1}) 2945, 1587, 1444, 1402, 1369, 1320, 1275, 1085, 1014, 833; MS (70

eV) m/z (rel. intensity) 219 (M^++1, 82), 218 (M^+, 100), 204 (63), 175 (100), 161 (74), 149 (62), 136 (60); exact mass cal. for $C_{15}H_{22}O$ 218.0944, found 218.1697.

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